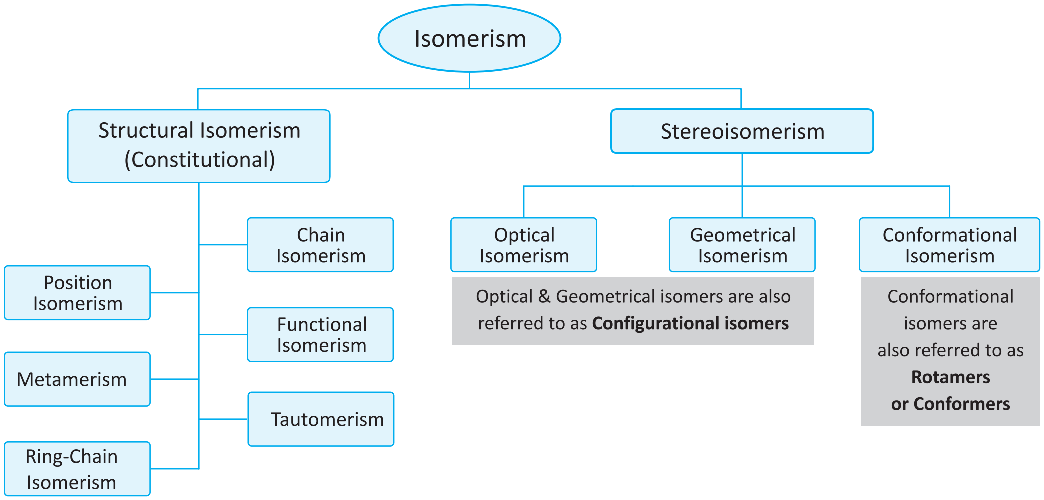
ISOMERISM IN ORGANIC COMPOUNDS Section - 4

Isomerism : The phenomenon of existence of two or more compounds possessing the same molecular formula but different chemical and physical properties is known as isomerism. Such compounds are individually referred to as isomers. For example : CH_3CH_2OH and CH_3OCH_3 are isomers of each other.

We have two types of isomerisms :

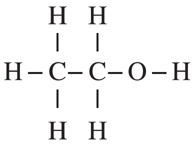
1. **Structural Isomerism :** These are also called as Constitutional Isomers.
2. **Stereo-Isomerism :**

Types of Isomerism :



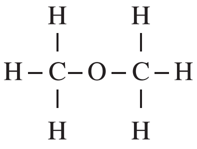
Structural Isomerism :

In this type of isomerism, the compounds possessing same molecular formula differ in their properties due to the difference in the linkage of atoms inside the molecule, i.e., due to the difference in their structures. For example: CH_3CH_2OH and CH_3OCH_3. Both have the molecular formula C_2H_6O but they differ in their structures (Ethanol has C–C–O linkage while Methoxymethane has C–O–C linkage).



$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-O-H$$

Ethanol



$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-O-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$$

Methoxymethane

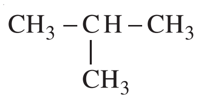
Structural isomers differ both in their physical as well as chemical properties.
Structural isomerism is classified into following six types.

1. **Chain Isomerism :** In this type of isomerism, the compounds possessing same molecular formula differ in their properties due to the difference in the arrangement of carbon chain present in them. In one of them the chain may be straight while in the other the chain may be branched.

- Butane (C_4H_{10}) has two chain isomers :

$CH_3-CH_2-CH_2-CH_3$

n-Butane



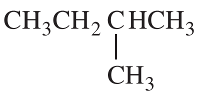
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_3$

Isobutane

- Pentane (C_5H_{12}) has three chain isomers :

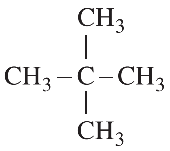
$CH_3CH_2CH_2CH_2CH_3$

n-Pentane



$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

Isopentane



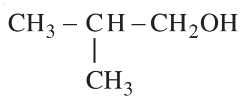
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

Neopentane

- Butyl alcohol (Butanol) has a chain isomer :

$CH_3-CH_2-CH_2-CH_2OH$

n-Butyl alcohol



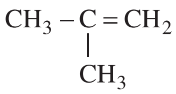
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2OH$

Isobutyl alcohol

- 1–Butene has a chain isomer :

$CH_3-CH_2-CH=CH_2$

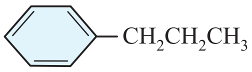
But-1-ene



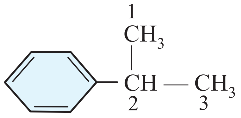
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$

Isobutene

- Aromatic Compounds may also have chain isomers :



n – Propylbenzene



Isopropylbenzene

2. **Positional Isomerism :** In this type of isomerism, the compounds possessing same molecular formula differ in their properties due to the difference in the position of either the functional group or the multiple bond or the branched chain attached to the main carbon chain. For example :

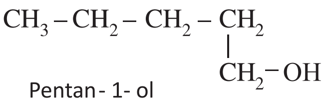
- Pentan-2-ol and Pentan-3-ol are the positional isomers :

$CH_3-CH_2-CH_2-CH(OH)-CH_3$

Pentan- 2- ol

$CH_3-CH_2-CH(OH)-CH_2-CH_3$

Pentan- 3- ol



$CH_3-CH_2-CH_2-\underset{\displaystyle CH_2-OH}{\underset{|}{CH_2}}$

Pentan- 1- ol

- Butene has two position isomers :

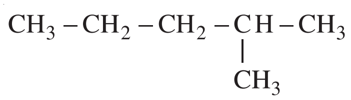
$CH_3-CH_2-CH=CH_2$

But-1-ene

$CH_3-CH=CH-CH_3$

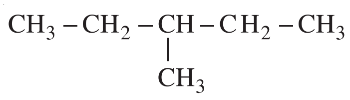
But-2-ene

- Methylpentane has position isomers :



$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3$

2-Methylpentane



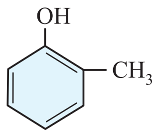
$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2-CH_3$

3-Methylpentane

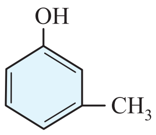
Note that the position isomers have the same parent carbon chain.

- In aromatic compounds, for example, in benzene ring three different positions are possible for a disubstituted product. They are 1–2 (called as ortho), 1–3 (called as meta), and 1–4 (called as para). Disubstituted benzene has three positional isomers. For example :

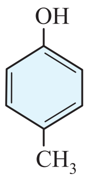
- Cresol has three positional isomers.



o-Cresol



m-Cresol



p-Cresol

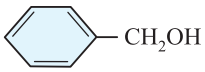
3. **Functional Isomerism :** In this type of isomerism the compounds possessing same molecular formula differ in their properties due to the difference in their functional group, i.e., the functional isomers differ in the functional group present in them. For example :

- Alcohols (except methanol) have their isomeric ethers.

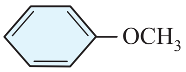
eg. Ethyl alcohol and Dimethyl ether having molecular formula of C_2H_6O are functional isomers :

CH_3CH_2OH
Ethanol

$H_3C–O–CH_3$
Methoxymethane



Benzyl alcohol



Anisole (Methylphenyl ether)

- Aldehydes have isomeric ketones.

Propionaldehyde (Propanal) and Acetone (Propanone) are functional isomers:

CH_3CH_2CHO
Propanal

CH_3COCH_3
Propanone

Methanal, Ethanal, and Benzaldehyde have no isomeric ketones.

- An acid may be isomeric to an ester.

Propionic acid and Methyl acetate (Methyl ethanoate) are functional isomers:

CH_3CH_2COOH
Propanoic acid

CH_3COOCH_3
Methyl ethanoate

Only Methanoic acid cannot have its isomeric ester.

Note that sometimes an alkadiene may be isomeric with an alkyne. This is also called as functional isomerism.

- Butyne is isomeric to Butadiene :

$CH_3-CH_2-C\equiv CH$
But-1-yne

$H_2C=CH-CH=CH_2$
Buta-1, 3-diene

- Unsaturated alcohols are isomeric to Aldehydes :

$H_2C=CHOH$ Vinyl Alcohol

CH_3CHO Acetaldehyde

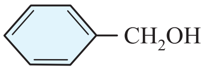
- Unsaturated alcohols containing three or more carbon atoms are isomeric to Aldehydes as well as Ketones :

$CH_2=CH-CH_2OH$ Allyl alcohol

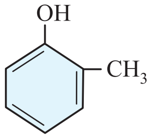
CH_3CH_2CHO Propionaldehyde

CH_3COCH_3 Acetone

- Aromatic alcohols may be isomeric to Phenols :



Benzyl alcohol

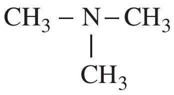


o-Cresol

- Primary, Secondary, and Tertiary amines of same molecular formula are functional isomers :

$CH_3CH_2CH_2NH_2$ n-Propyl amine (1°)

$CH_3-NH-C_2H_5$ Ethyl methyl amine (2°)


$CH_3-N(CH_3)-CH_3$

Trimethyl amine (3°)

4. **Metamerism :** In this type of isomerism the compounds possessing same molecular formula differ in their properties due to the difference in alkyl groups present in them. Thus, the metamers differ only in the alkyl groups present and they have same functional group, i.e., they belong to same homologous series. For example :

- Diethyl ether (Ethoxyethane) and Methyl propyl ether (Methoxypropane) are metamers :

$C_2H_5-O-C_2H_5$ Ethoxy ethane

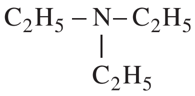
$CH_3-O-C_3H_7$ Methoxy propane

- Diethylamine and Methylpropylamine are also metamers :

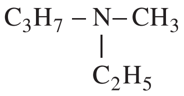
$C_2H_5-NH-C_2H_5$ Diethyl amine

$CH_3-NH-C_3H_7$ Methyl propyl amine

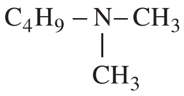
- Metamers of 3° amines ($C_6H_{15}N$) :


$C_2H_5-N(C_2H_5)-C_2H_5$

Triethyl amine


$C_3H_7-N(C_2H_5)-CH_3$

Ethyl methyl propyl amine


$C_4H_9-N(CH_3)-CH_3$

Dimethyl butyl amine

- Esters also show metamerism, n-Propyl formate has Ethyl acetate and Methyl propionate as its metamers.

$HCOOC_3H_7$ n-Propyl formate

$CH_3COOC_2H_5$ Ethyl acetate

$CH_3CH_2COOCH_3$ Methyl propionate

5. **Tautomerism :** This is a special case of functional isomerism. In this type of isomerism two functional isomers exist together in equilibrium. The two forms existing in equilibrium are called as tautomers. For example :

- Consider tautomerism in Acetaldehyde (keto group) and Vinyl alcohol (enol group).

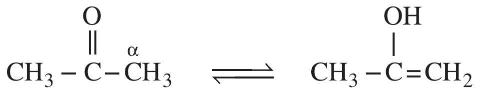
$$\underset{\text{Acetaldehyde}}{CH_3CHO} \rightleftharpoons \underset{\text{Vinyl alcohol}}{H_2C=CHOH}$$

Out of the two tautomeric forms, generally the keto form is more stable and exists in larger proportion. The equilibrium between the two forms is dynamic, i.e., if one form is somehow removed by a reaction, some of the amount of the other form changes into the first form so that similar equilibrium exists again.

Due to the presence of keto and enol form this type of tautomerism is known as keto-enol tautomerism. It is the most commonly observed type of tautomerism.

The keto-enol tautomerism is possible only in those Ketones and Aldehydes in which at least one α-hydrogen atom is present so that it may convert the carbonyl group to enol group.

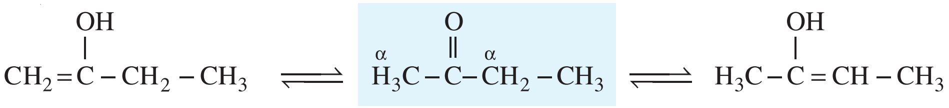
- Consider the compound Acetone. it has two tautomers, one has a keto group and other has an enol group.



$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{C}H_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH_2$$

Keto - form Enol - form

- Another example of keto–enol tautomerism is observed in 2-Butanone. It has two enol forms,



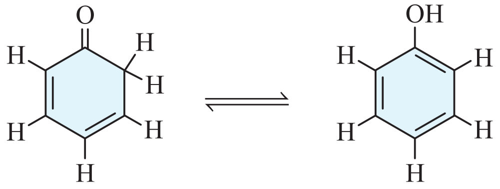
$$CH_2=\overset{\overset{OH}{|}}{C}-CH_2-CH_3 \rightleftharpoons \overset{\alpha}{H_3C}-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{CH_2}-CH_3 \rightleftharpoons H_3C-\overset{\overset{OH}{|}}{C}=CH-CH_3$$

Hence it is observed that (as above), if the α-hydrogen atoms are present on both the carbons attached to carbonyl group, it can have more than one enol. Thus, larger the number of different α-hydrogens in a ketone, more is the number of enols. In most of the cases, the keto form is more stable than the enol by some 45–60 kJ/mol (11–14 kcal/mol). The main reason for this difference is that a carbon–oxygen double bond is stronger than a carbon–carbon double bond.

Stabilized Enols :

Certain structural features can make the keto-enol equilibrium more favourable by stabilizing the enol form such as extended conjugation, intramolecular H-bonding and aromatic characters etc.

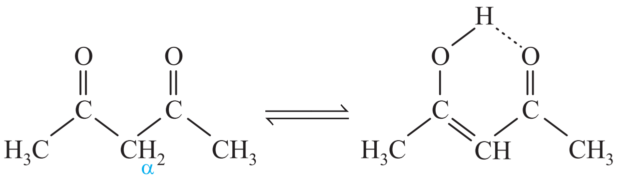
2, 4-Cyclohexadienone
(keto form; not aromatic)



Phenol
(enol form; aromatic)

The enol form is phenol, and the stabilization gained by forming an aromatic ring is more than enough to overcome the normal preference for the keto form.

The 1, 3 arrangement of two carbonyl groups in β-diketones leads to a situation in which the keto and the enol forms are of comparable stability.



2, 4-Pentanedione
(keto form)

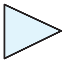
4-Hydroxy-3-pentene-2-one
(enol form)

6. **Ring chain isomerism :** Compounds having the same molecular formula but possessing open chain and cyclic structures are called ring chain isomers and the phenomenon is called ring chain isomerism. For example:

- Alkenes are isomeric with Cycloalkanes :

$CH_3CH=CH_2$

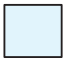
Propene



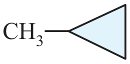
Cyclopropane

$CH_3CH_2CH=CH_2$

But-1-ene



Cyclobutane



Methyl cyclopropane

- Alkynes and Alkadienes are isomeric with Cycloalkenes :

$CH_3CH_2C\equiv CH$

But-1-yne

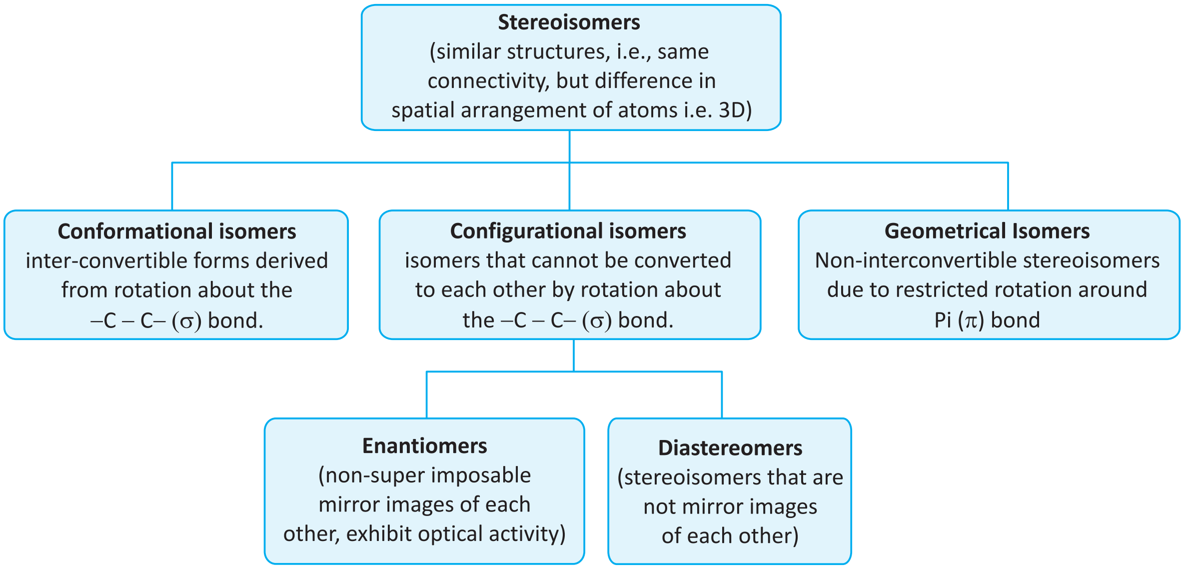
$CH_2=CH-CH=CH_2$

Buta-1, 3-diene

Cyclobutene

Stereo-isomerism :

The stereoisomerism is defined as the type of isomerism in which compounds possessing same molecular formula and same structural formula, differ in their properties due to the difference in the arrangement in space of their atoms in the molecule. Stereoisomers usually differ in some of their physical properties but they may not differ much in their chemical properties.



Stereoisomers
(similar structures, i.e., same connectivity, but difference in spatial arrangement of atoms i.e. 3D)

Conformational isomers
inter-convertible forms derived from rotation about the $-C-C-$ (σ) bond.

Configurational isomers
isomers that cannot be converted to each other by rotation about the $-C-C-$ (σ) bond.

Geometrical Isomers
Non-interconvertible stereoisomers due to restricted rotation around Pi (π) bond

Enantiomers
(non-super imposable mirror images of each other, exhibit optical activity)

Diastereomers
(stereoisomers that are not mirror images of each other)

In order to understand stereoisomerism, we need to familiarize ourselves with the following concepts.

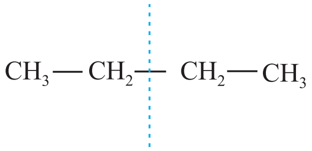
Chirality

A molecule or any other object that cannot be superimposed onto its mirror image is said to be chiral, and the phenomenon is known as chirality. Chirality arises from asymmetry in a molecule.

Objects and molecules that are super-imposable on their mirror images are achiral.

A test for chirality is to look for a plane of symmetry in the molecule. If there exists such a plane of symmetry that divides the molecule into two identical halves, then such a molecule is achiral.

for e.g. n-butane is achiral while 2-chlorobutane is chiral.



$CH_3-CH_2-CH_2-CH_3$

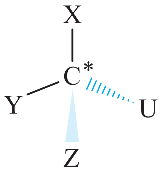
Plane of symmetry
n-Butane - ACHIRAL

$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_3$

No plane of symmetry
2-Chlorobutane - CHIRAL

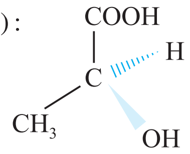
Stereocentre - An Asymmetric Carbon

A sp^3 hybridised carbon atom that is bonded to four different substituents or groups (including hydrogen) is a stereocentre.



[$X \neq Y \neq Z \neq U$; * stereocentre or chiral centre]

For example, consider Lactic acid (2-Hydroxy propanoic acid) :



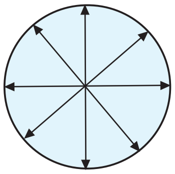
A molecule with only one stereocentre will be chiral, because such a molecule does not possess a plane of symmetry and hence is non-super imposable on its mirror image.

Note : Molecules containing more than one stereocentre may or may not exhibit chirality depending on whether they have a plane of symmetry and are superimposable on their mirror images or not.

Plane Polarized Light

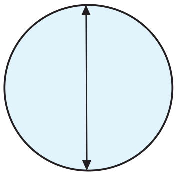
Light is an electromagnetic wave, with oscillating electric and magnetic fields.

If we were to view a beam of ordinary light from one end, and if we could actually see the planes in which the electrical oscillations were occuring, we would find that oscillations of the electric field were occuring in all possible-planes, perpendicular to the direction of propagation. (The same would be true for magnetic field)



Un-polarised light

Oscillations of the electric field of ordinary light occur in all possible planes, perpendicular to the direction of propagation [Note that the direction of propagation is perpendicular to the plane of paper].



Plane-polarised light

When ordinary light is passed through a polarizer like Nicole prism, the light that emerges from the polarizer is oscillating only in one plane. Such light is called plane-polarized light. In the given figure, the plane of oscillation of the electric field of plane-polarized light is vertical.

Optical Activity

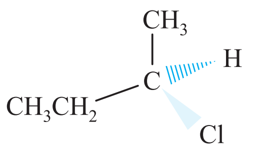
It is found that some compounds have a tendency to rotate the plane of plane-polarized light, i.e., when any such compound is placed in the path of plane-polarized light, the compound rotates the plane of this light by a certain angle. Such a rotation is known as optical rotation, and the phenomenon is called Optical Activity.

This optical rotation may be clockwise (+) or anti-clockwise (-). The molecules rotating the plane in clockwise direction are termed as dextro-rotatory (d) or (+), while the molecules rotating the plane in anti-clockwise direction are termed as laevo-rotatory (*l*) or (-). The instrument used to measure optical rotation is called as Polarimeter.

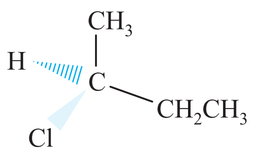
Optical activity is a characteristic of chiral molecules only. We know that a chiral molecule is one that cannot be superimposed on its mirror image. Such a molecule and its non-super imposable mirror image form a pair of enantiomers.

Enantiomers rotate the plane of plane polarized light to the same extent but in opposite direction, i.e., one of them is dextro-rotatory and the other is laevo-rotatory.

Consider 2-Chlorobutane, $CH_3-CH(Cl)-CH_2CH_3$.



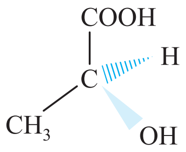
(+)-2-Chlorobutane



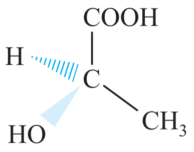
(-)-2-Chlorobutane

Whether a compound is dextro-rotatary or laevo-rotatory can only be determined experimentally, and not by merely looking at the 3-D structure of the compound.

Another very common example is of Lactic Acid, $CH_3-CH(OH)-COOH$.



(+)-Lactic Acid



(–)-Lactic Acid

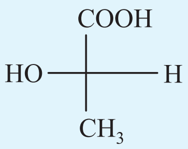
Note : Any dissymmetric compound having non-superimposable mirror image is optically active compound.

Racemic Mixture :

An equimolecular mixture of (+) and (-) (i.e., *d*-and *l*-) forms of an optically active compound is not able to rotate the plane of plane-polarized light because of the mutual cancellation. Such a mixture is known as a Racemic mixture or dl-mixture (±) mixture and is optically inactive. The phenomenon is called racemization. Thus, lactic acid can be said to be of three types, i.e., (+) lactic acid, (-) lactic acid, and (±) lactic acid.

Note :

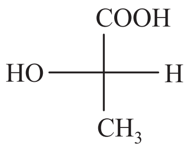
- Representation of a molecule in tetrahedral three dimensional shapes is a little bit difficult. A simplified way to represent such molecules on plane of paper is by using the *Fischer projection formula*. In a Fischer projection formula, (+) lactic acid is represented as :



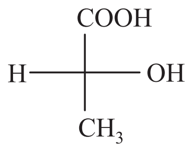
$$\begin{array}{ccc} & \text{COOH} & \\ & | & \\ \text{HO} & — & \text{H} \\ & | & \\ & \text{CH}_3 & \end{array}$$

- Fischer projection formula can't be rotated by 90° and can't be lifted from the plane of the paper.

The chiral carbon atom is represented by a point of intersection of a horizontal and a vertical line. Atoms or groups attached with horizontal line are supposed to be coming forward above the plane of paper (i.e., towards the viewer) while the groups attached with vertical line are going back behind the plane of paper (away from the viewer). Thus, the two enantiomers of lactic acid are represented as follows :



(+) Lactic acid



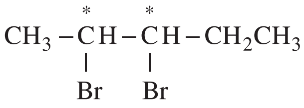
(–) Lactic acid

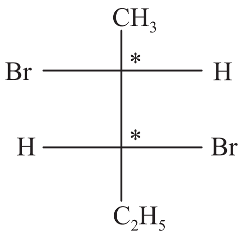
Compounds Containing Two Stereocentres

A useful rule gives the maximum number of stereoisomers of a compound.

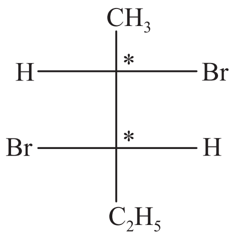
Total number of stereoisomers = 2^n (only configurational), where n = number of stereocentres in the molecule.

So, a molecule with 2 stereocentres can have a maximum of $2^2 = 4$ stereoisomeric forms.

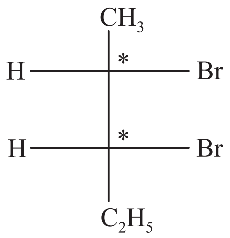
Consider 2, 3-Dibromopentane,  $CH_3-\underset{\displaystyle Br}{\underset{|}{\overset{*}{C}}}H-\underset{\displaystyle Br}{\underset{|}{\overset{*}{C}}}H-CH_2CH_3$ has 4 stereoisomers as shown below.



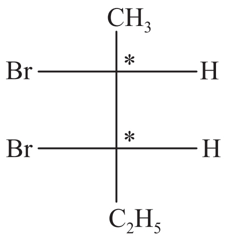
(I)



(II)



(III)



(IV)

- Enantiomers are non-super imposable mirror images.
- Diastereomers are non-super imposable non-mirror images.

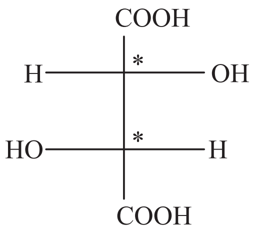
Note that the pairs I & II and III & IV form pairs of Enantiomers (Optical Isomers).

And pairs I and III and I and IV and II and III etc. form pairs of diastereomers.

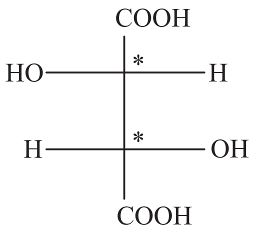
Meso Compounds and Diastereomers

A structure with two stereocentres does not always have four possible stereoisomers. Sometimes, there are only three. This happens because some molecules are achiral even though they contain stereocentres. To understand this, let us consider the example of tartaric acid : HOOC – CH(OH) – CH(OH) – COOH

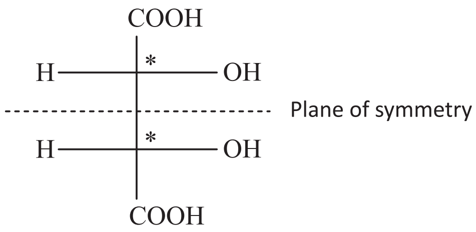
Tartaric Acid has only three stereomers.



I
(+) Tartaric Acid



II
(–) Tartaric Acid



III
meso- Tartaric Acid

I and II are non-superimposable mirror images of each other (ENANTIOMERS).

If we look at structure III, it also has 2 stereocentres. But we can also note the presence of a plane of symmetry in it. As described earlier, such a molecule is achiral, despite the presence of 2 stereocentres, and it shall be super imposable on its mirror image. Such an isomer, which has stereocentres, but the molecule is overall Achiral is called a meso-isomer.

Note : Observe that in the case of 2, 3-Dibromopentane (above), there is no plane of symmetry in either of stereomers.

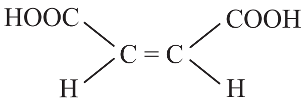
Note : (i) The meso compound and its mirror image both represent a single configuration (i.e., one isomer)

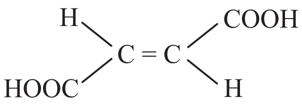
(ii) The meso-isomer is optically inactive (achiral). In the meso-isomer, half part of the molecule gives clockwise while the other half gives anti-clockwise rotation (due to a plane of symmetry), and thus, because of internal compensation, the molecule is optically inactive. While the racemic mixture is not able to show optical rotation because of external compensation, the meso form is not able to show any rotation because of internal compensation.

(iii) The meso-tartaric acid is not the enantioner of either I or II forms. The molecules (configurations) which are not mirror images of one another are called diastereomers. The meso-tartaric acid is a diastereomer of I and II forms of tartaric acid.

Geometrical Isomerism

Consider the compound, 2-Buten-1, 4-dioic acid, HOOC – CH = CH – COOH. This compound can be expressed in two different forms as follows :

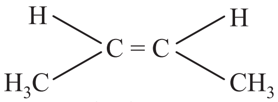

Maleic Acid

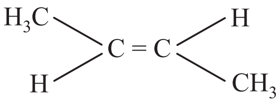

Fumaric Acid

Since free rotation about C = C Pi (π) bond is not allowed, these two geometries are non-inter convertible and different. These are geometrical isomers of each other.

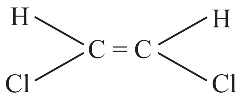
In Maleic acid, both –COOH groups are attached in the same direction, while in Fumaric acid, the two –COOH groups are attached in opposite direction. The geometrical isomer in which the similar groups are present in same direction (on the same side of double bond) is called as the *cis isomer*, while the one in which similar groups are in opposite direction is called as the *trans isomer*. Geometrical isomerism is also known as *cis-trans* isomerism. Maleic acid is the *cis* isomer while Fumaric acid is the *trans* isomer.

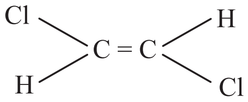
- 2–Butene also exhibits geometrical isomerism :


cis - isomer


trans - isomer

- 1,2–Dichloroethene is another example of geometrical isomerism :


cis - isomer

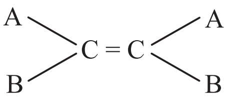

trans - isomer

- Note that an organic compound having a $>C = C<$ bond may or may not show geometrical isomerism.

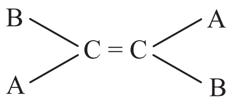
  If two similar groups (or atoms) are attached to same carbon atom (forming a double bond) in a compound, then it does not show geometrical isomerism.

An organic compound having $>C = C<$ can have the following different forms :

I.

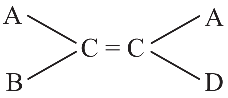


cis - isomer

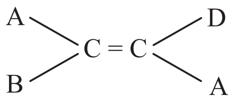


trans - isomer

II.



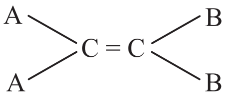
cis - isomer



trans - isomer

Such compounds show geometrical isomerism and we can classify them as having *cis* and *trans* forms.

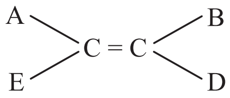
III.



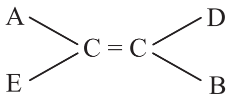
Such compounds where 2 similar groups are attached to one carbon atom, do not show geometrical isomerism.

Important Alkenes which do not show geometrical isomerism include Ethene ($CH_2 = CH_2$), Propene ($CH_3CH = CH_2$), 1-Butene ($C_2H_5CH = CH_2$), Isobutene ($Me_2C = CH_2$) and Styrene ($C_6H_5CH = CH_2$).

IV.



and

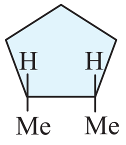


Such a pair of compound are geometrical isomers, but cannot be classified as *cis-trans*.

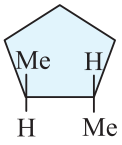
Note : *cis* form is comparatively less stable because of the mutual repulsion between the groups. Thus, Maleic acid is less stable than Fumaric acid. Geometrical isomers differ in their physical properties and also in some of their chemical properties. The *trans* form, being symmetrical has a zero dipole moment. Even in the cases when the trans form is not symmetrical, it has a low dipole moment in comparison to the cis form. Since the trans form is less polar, it is less soluble in water. Also, being polar the cis isomer has comparatively higher boiling point. However, melting point of trans isomer is higher because of better packing in crystal due to symmetry in molecule. Besides, the cis isomer has higher heat of hydrogenation, heat of combustion, density, and refractive index. Accordingly, Fumaric acid has higher melting point and is very sparingly soluble in water in comparison to Maleic acid.

Geometrical Isomerism in Cyclic Compounds :

In cyclic compounds the rotation about a C–C single bond is not free because of the rigidity caused by the presence of other carbons of the ring which keep them tightly held. Thus, a disubstituted cyclic compound (having two substitutions at separate carbons) will exist as geometrical isomers. For example, consider 1, 2-Dimethylcyclopentane :

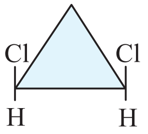


cis-1, 2-Dimethylcyclopentane

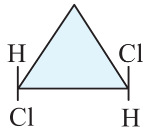


trans-1, 2-Dimethylcyclopentane

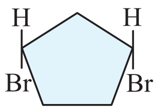
Other examples of Cycloalkanes and their derivatives showing Geometric Isomerism are illustrated below :



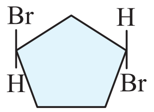
cis-1, 2-Dichlorocyclopropane



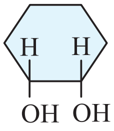
trans-1, 2-Dichlorocyclopropane



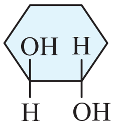
cis - 1, 3-Dibromocyclopentane



trans - 1, 3-Dibromocyclopentane



cis-Cyclohexane-1, 2-diol



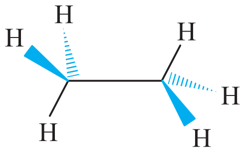
trans-Cyclohexane-1, 2-diol

Conformational Isomerism :

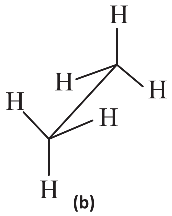
Conformations are different spatial arrangements of a molecule that are generated by rotation about single bonds. Conformational analysis is the study of how conformational factors affect the structure of a molecule and its physical and chemical properties.

I. **Conformational analysis of Ethane :** Ethane is the simplest hydrocarbon that can have distinct conformations. These two conformations are the staggered conformation and the eclipsed conformation. In the staggered conformation, each C – H bond of one carbon bisects an H – C – H angle of the other carbon.

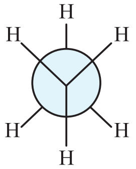
Some commonly used drawings of the staggered conformation of ethane.



(a)
Wedge - and - dash

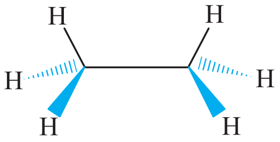


(b)
Saw horse

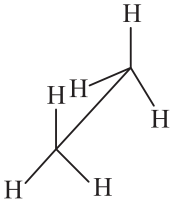


(c)
Newman projection

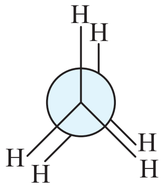
In the eclipsed conformation, each C – H bond of one carbon is aligned with a C – H bond of the other carbon. Some commonly used drawings of the eclipsed conformation of ethane.



(a)
Wedge - and - dash



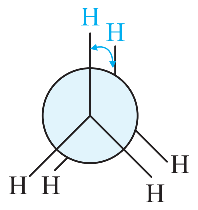
(b)
Saw horse



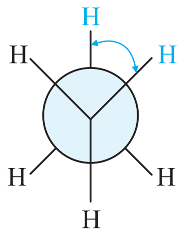
(c)
Newman projection

Note : In a Newman projection (figure C), we sight down the C – C bond, and represent the front carbon by a point and the back carbon by a circle. Each carbon has three other bonds that are placed symmetrically around it.

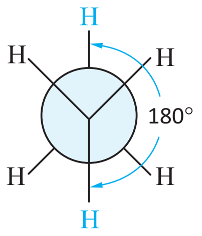
The structural feature that above mentioned figure illustrate is the spatial relationship between atoms on adjacent carbons. Each H – C – C – H unit in ethane is characterized by a torsion angle or dihedral angle, which is the angle between the H – C – C plane and the C – C – H plane. The dihedral angle is easily seen in a Newman projection of ethane as the angle between C – H bonds of adjacent carbons.



Dihedral angle = 0°
Eclipsed



Dihedral angle = 60°
Gauche



Dihedral angle = 180°
Anti

Note : The staggered conformations have only gauche or anti-relationship between bonds on adjacent atoms.

The staggered and eclipsed conformation inter convert by rotation around the C – C bond, and do so very rapidly.

Note : Different conformations of the same compound are sometimes called conformers or rotamers. Of the two conformations of ethane, the staggered is 12 kJ/mol more stable than the eclipsed. The staggered conformation is most stable conformations; the eclipsed is the least stable conformation.

Conformations in which the dihedral angle between adjacent bonds are other than 60° are said to have torsional strain. Eclipsed bonds produce the most torsional strain ; staggered bonds none.

Note : In principle ethane has an infinite number of conformations that differ by only tiny increments in their dihedral angle. Not only is the staggered conformation more stable than the eclipsed, it is the most stable of all of the conformations ; the eclipsed is the least stable.

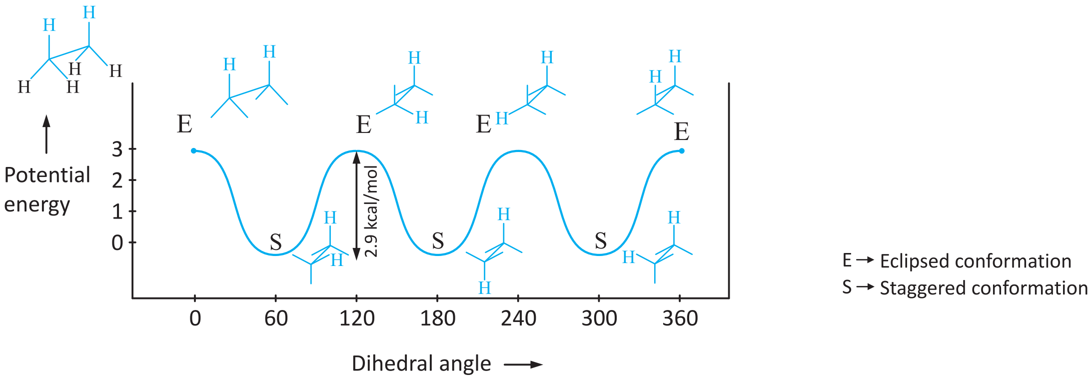
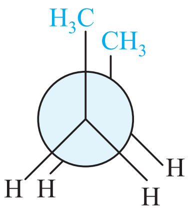


Figure : Potential energy diagram for rotation about the carbon-carbon bond in ethane

II. Conformational Analysis of Butane :

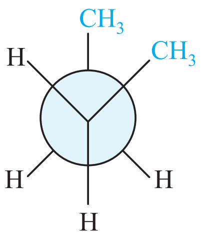
We consider conformations related by rotation about the bond between the middle two carbon ($CH_3CH_2 – CH_2CH_3$). Butane has four main conformations [two eclipsed type and two staggered type].

Unlike ethane, in which the staggered conformations are equivalent, two different staggered conformations occur in butane.



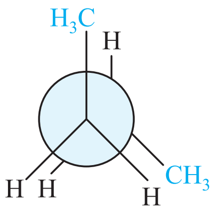
[I]

Fully Eclipsed



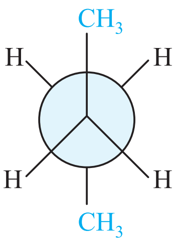
[II]

Gauche



[III]

Partially Eclipsed

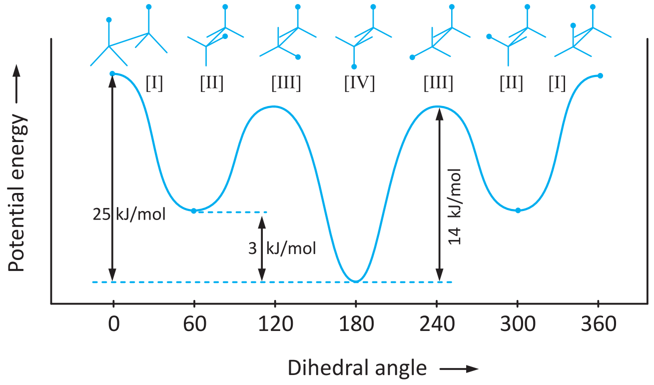


[IV]

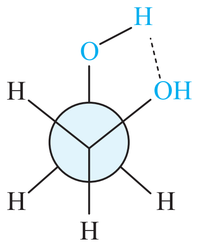
Anti

The gauche conformation and anti-conformation both are staggered, so are free of torsional strain, but two of the methyl hydrogens of the gauche conformations lie within 210 pm of each other. This distance is less than the sum of their van der Waals radii (240 pm), and there is a repulsive force between them. The destabilization of a molecule that results when two of its atoms are too close to each other is called van der Waals strain, or steric hinderance and contributes to the total steric strain.

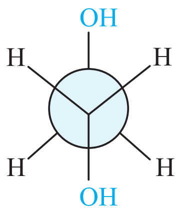
In the case of butane, van der Waals strain makes the gauche conformation approximately 0.8 kcal/mol less stable than the anti.



***Note* :** For ethane-1, 2-diol (ethylene glycol HO – CH_2 – CH_2 – OH) gauche conformation is more stable than the anti-conformation because of H-bonding in gauche conformation.



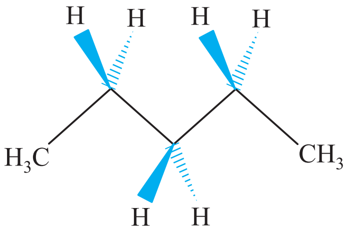
Gauche conformation



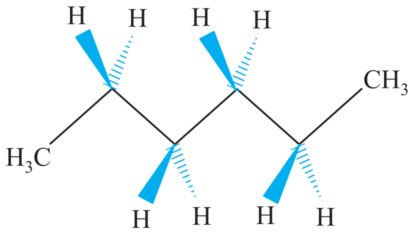
Anti conformation

III. Conformations of Higher alkanes :

Higher alkanes having unbranched carbon chain are, like butane, most stable in their all-anti conformations. In depicting the conformations of higher alkanes it is often more helpful to look at them from the side rather than end-on as in Newman projection. Viewed from this perspective, the most stable conformations of pentane and hexane have their carbon “backbones” arranged in a zig-zag fashion as shown in the figure. All the bonds are staggered, and the chain are characterized by anti-arrangements of C – C – C – C units.

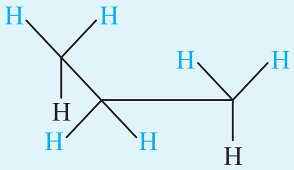


Pentane

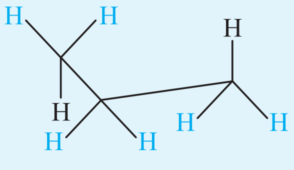


Hexane

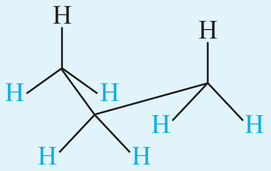
Illustration - 4 *Of the three conformations of propane shown, which one is the most stable? Which one is the least stable? Why?*



(A)



(B)



(C)

SOLUTION :

Conformation (A) is the most stable ; all its bonds are staggered. Conformation (C) is the least stable ; all its bonds are eclipsed.

Illustration - 5 *Sight down the C-2 – C-3 bond, and draw Newman projection formulas for the :*

(a) *Most stable conformation of 2, 2-dimethyl butane.*

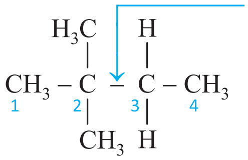
(b) *Two most stable conformations of 2-methyl butane.*

(c) *Two most stable conformations of 2, 3-dimethyl butane.*

(d) *One of the two staggered conformations of 2-methyl butane is more stable than the other. Which one is more stable ? Why?*

SOLUTION :

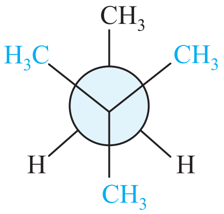
(a) First write out the structural formula of 2, 2-dimethyl butane in order to identify the substituent groups attached to C-2 and C-3.



$$\underset{1}{CH_3} - \underset{2}{\overset{H_3C}{\underset{CH_3}{C}}} \overset{\downarrow}{-} \underset{3}{\overset{H}{\underset{H}{C}}} - \underset{4}{CH_3}$$

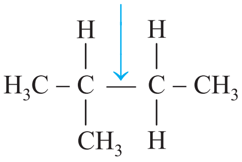
Sight along this bond

As shown in above structure C-2 bears three methyl groups, and C-3 bears two hydrogens and a methyl group. The most stable conformation is the staggered one as shown below. All other staggered conformations are equivalent to this one.

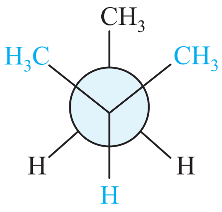


(b) The constitution of 2-methylbutane and its two most stable conformations are shown.

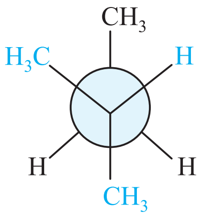
Sight along this bond



$$H_3C - \overset{H}{\underset{CH_3}{C}} \overset{\downarrow}{-} \overset{H}{\underset{H}{C}} - CH_3$$



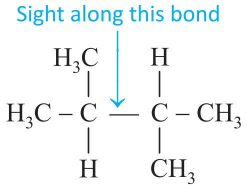
(X)



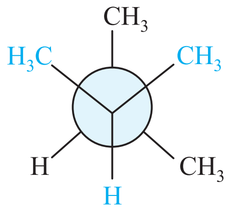
(Y)

Both conformations are staggered. In one Newman projection (X), the methyl group at the back is gauche to the two methyl groups in the front. In the other (Y), it is gauche to one and anti to the other.

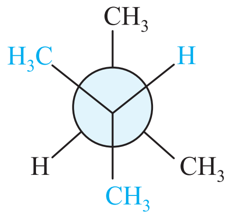
(c) The hydrogens at C-2 and C-3 may be gauche to one another (P), or they may be anti (Q).


Sight along this bond

$$\begin{array}{ccc} H_3C & & H \\ | & & | \\ H_3C-C & — & C-CH_3 \\ | & & | \\ H & & CH_3 \end{array}$$

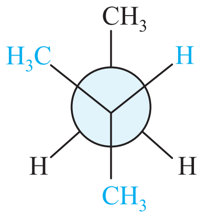


(P)

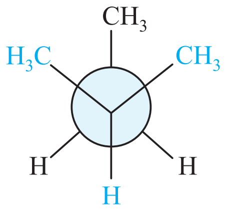


(Q)

(d) The 2-methylbutane conformation with one gauche $CH_3 \ldots . CH_3$ and one anti $CH_3 \ldots . CH_3$ relationship is more stable than the one with two gauche $CH_3 \ldots . CH_3$ relationships. The more stable conformation has less van der Waals strain.



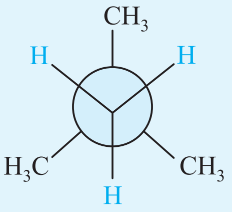
(More stable)



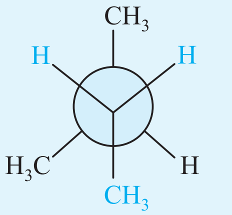
(Less stable)

Illustration - 6 *Determine whether the two/three structures in each of the following pairs represent constitutional (structural) isomers or different conformations of the same compound.*

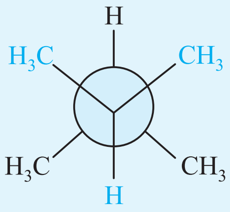
(a)



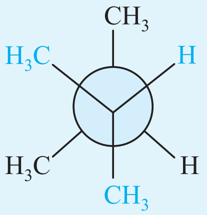
and



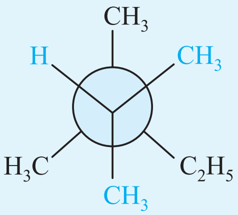
(b)



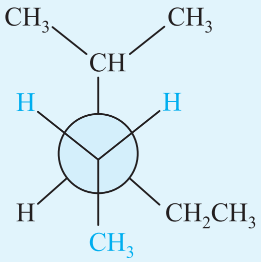
and



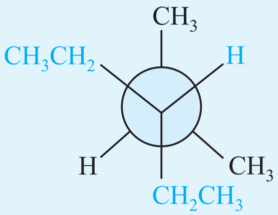
(c)



[I]



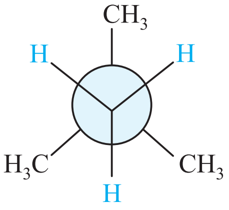
[II]



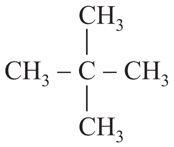
[III]

SOLUTION :

(a) By rewriting the structures in a form that shows the order of their atomic connections, it is apparent that the two structures are constitutional (structural) isomers.

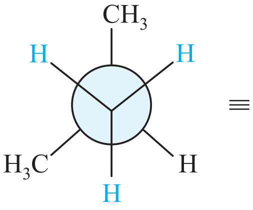


$\equiv$

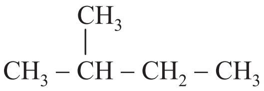


$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array}$$

2, 2-Dimethylpropane



$\equiv$



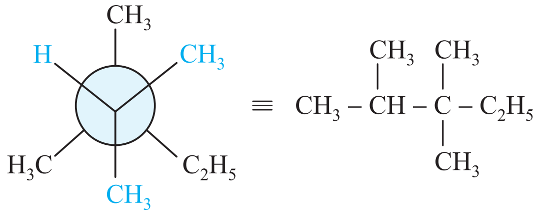
$$\begin{array}{l} \quad\;\; CH_3 \\ \quad\;\; | \\ CH_3-CH-CH_2-CH_3 \end{array}$$

2-Methylbutane

(b) The two compounds have the same constitution (structure) ; both are $(CH_3)_2CHCH(CH_3)_2$. The Newman projections represent different staggered conformations of the same molecule ; in one the hydrogens are anti to each other whereas in the other they are gauche. Both are different conformations of 2, 3-dimethylbutane.

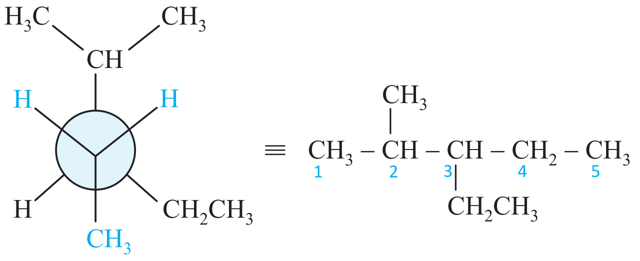
(c) I and II are constitutional isomers.

II and III are two Newman's projection formula of the same compound 3-Ethyl-2-methylpentane hence these are same. II is Newman's projection formula about C-3 – C-4 bond while III is Newman's projection formula about C-2 – C-3 bond.



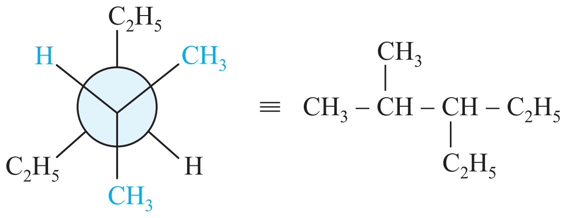
$$\equiv CH_3-\overset{CH_3}{CH}-\underset{CH_3}{\overset{CH_3}{C}}-C_2H_5$$

I.



$$\equiv \underset{1}{CH_3}-\underset{2}{\overset{CH_3}{CH}}-\underset{3}{\underset{CH_2CH_3}{CH}}-\underset{4}{CH_2}-\underset{5}{CH_3}$$

II.



$$\equiv CH_3-\overset{CH_3}{CH}-\underset{C_2H_5}{CH}-C_2H_5$$

III.

Illustration - 7 *Write a structural formula for the most stable conformation of 2, 2, 5, 5-tetramethyl hexane using Newman's projection of conformation about C-3 – C-4 bond.*

SOLUTION :

The structural formula of compound is $(CH_3)_3CCH_2CH_2C(CH_3)_3$. Both C-3 and C-4 have two hydrogens and a tert-butyl groups attached. The most stable conformation has the large tert-butyl groups anti to each other.

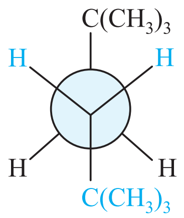


Illustration - 8 **(a)** *Write Newman projections for the gauche and anti conformations of 1, 2-dichloro ethane ($Cl-CH_2\,CH_2-Cl$).*

(b) *The measured dipole moment of $ClCH_2CH_2Cl$ is 1.12D. Which one of the following statements about 1, 2-dichloroethane is false ?*

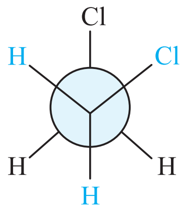
(i) *It may exist entirely in the anti-conformation*

(ii) *It may exist entirely in the gauche conformation.*

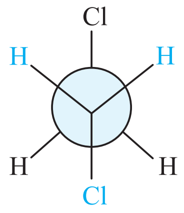
(iii) *It may exist as a mixture of anti and gauche conformations.*

SOLUTION :

(a) The dihedral angle between chlorine substituents is 60° in the gauche conformation and 180° in the anti conformation of $Cl-CH_2-CH_2-Cl$.



Gauche



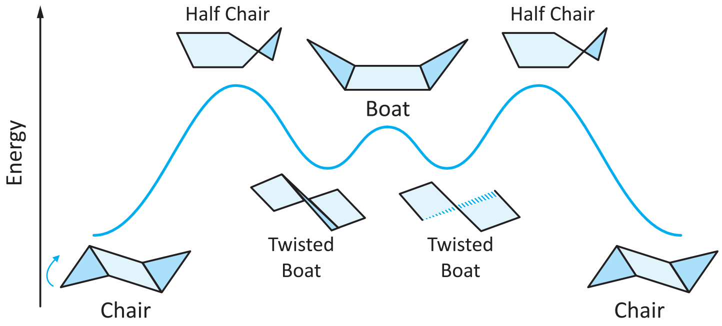
Anti

(b) All the individual bond dipole moments cancel in the anti conformation of $Cl-CH_2-CH_2-Cl$, and this conformation has no dipole moment. Because $ClCH_2CH_2Cl$ has a dipole moment of 1.12D, it can exist entirely in the gauche conformation or it can be a mixture of anti and gauche conformations, but it cannot exist entirely in the anti conformation. Statement 1 is false.

Conformers of Cyclohexane :

The cyclic compounds most commonly found in nature contain six-membered rings because carbon rings of that size can exist in a conformation - called a chair conformer - that is almost completely free of strain.

Cyclohexane can also exist as a boat conformer, shown in figure like the chair conformer, the boat conformer is free of strain. However, the boat conformer is not as stable because some of the bonds are eclipsed.



Order of Stability : Chair form > Twisted boat > Boat > Half chair.

IN-CHAPTER EXERCISE-B

1. *Write structural formulae for each of the following* :

(i) *Three primary alcohols and one tertiary alcohol with the formula* C_4H_8O

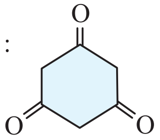
(ii) *A secondary alcohol with the formula* C_3H_6O

(iii) *A cyclic ester with the formula* $C_4H_4O_4$

(iv) *Two unsaturated dibasic acids with formula* $C_4H_4O_4$

2. *Write all the isomers of the formula* $C_5H_{10}O_2$ *and the select pair of one type of isomers.*

3. *Make tautomer of* :



4. *Write structure that correspond to the following description* :

(i) *four esters with the formula* $C_4H_8O_2$

(ii) *two aldehydes with the formula* C_4H_8O

(iii) *three ketones with the formula* $C_5H_{10}O$

(iv) *a tertiary amine with the formula* $C_4H_{11}N$

Choose the correct alternative. Only One Choice is Correct :

5. *Which one of the following is chiral ?*

(A) 1, 1-*Dibromo*-1-*chloropropane*

(B) 1, 3-*Dibromo*-1-*chloropropane*

(C) 1, 1-*Dibromo*-3-*chloropropane*

(D) 1, 3-*Dibromo*-2-*chloropropane*

6. *How many geometrical isomers are possible for the following ?* $C_2H_5(CH_3)C = CHCH = CHCOOH$

(A) 1 **(B)** 2 **(C)** 3 **(D)** 4

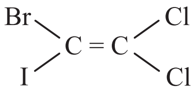
7. *Which of the following will have one of the stereoisomer as meso ?*

(A) 2-*chlorobutane* **(B)** 2, 3-*dichlorobutane*

(C) 2, 3-*dichloropentane* **(D)** 2-*hydroxypropanoic acid*

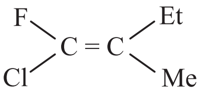
8. *Which of following compound can show geometrical isomerism ?*

(I)

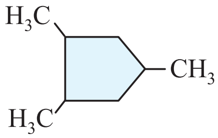


(II) DHC = CHD (D:Deuterium)

(III)



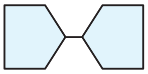
(IV)



The correct option is :

(A) *I, II* **(B)** *I, II, III* **(C)** *II, III, IV* **(D)** *I, II, III, IV*

9. (A) $\xrightarrow{H_2(1\text{ mole})/Pt}$



Double bond equivalent (degree of Unsaturation) of (A) is :

(A) 1 **(B)** 2 **(C)** 3 **(D)** 4

10. *Select the response that correctly identifies the number of carbon atoms of each type of hybridization in the compound given below* $H_2C = C = CH—CH = O$

	sp^3	sp^2	sp		sp^3	sp^2	sp
(A)	0	4	0	**(B)**	0	2	2
(C)	0	3	1	**(D)**	1	3	0

11. *Which of the following show geometric isomerism ?*

(A) 1-*Phenyl*-2-*butene* **(B)** 3-*Phenyl*-1-*butene*

(C) 2-*Phenyl*-1-*butene* **(D)** 1, 1-*Diphenyl*-1-*propene*

12. Statement : 1 Compounds having only one chiral centre can have both enantiomer and diastereomer.

Statement : 2 Diastereomer may or may not have chirality.

(A) Statement-1 is True, Statement-2 is True and Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True and Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

***Note :** For Practice, please refer to questions given in Supplement-3 (Introduction to Organic Chemistry)